APPLICATIONS OF MASS PEAK PROFILING FROM SELECTED ION RECORDING DATA USING PROBE INTRODUCTION

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1. INTRODUCTION

The EPA, NERL, CRD in Las Vegas develops rapid characterization techniques for targeted analytes including Aroclors (commercial PCB mixtures) and PAHs. Also of interest are new techniques to help identify compounds. Mass peak profiling from selected ion recording data (MPPSIRD) acquired with a Fisons 70-250SE double focusing mass spectrometer using 10,000 to 20,000 resolution provides the high selectivity and sensitivity required.[1] Probe introductions of standard solutions and sample extracts were made to determine the utility of MPPSIRD for three rapid characterization applications.

2. Review of MPPSIRD

In Figure 1a, a full mass peak profile is shown. M/z ratios were monitored at each point and the areas of the chromatographic peak under each ion chromatogram were plotted to provide the profile. In Figure 1b, M, M+1 and M+2 partial profiles were plotted. Six m/z ratios were monitored across the top portion of each profile using a single SIR descriptor to provide exact masses for all three profiles and the abundances of the M+1 and M+2 partial profiles relative to the M partial profile. These values are used to test 5 criteria that eliminate all but the correct composition from a list of compositions possible for a given exact mass and mass error limit for M.[2] Once the composition of a molecular ion is known, the identity of the compound is limited to a finite number of isomers. For both types of data, the partial profile of a calibration ion is also monitored.

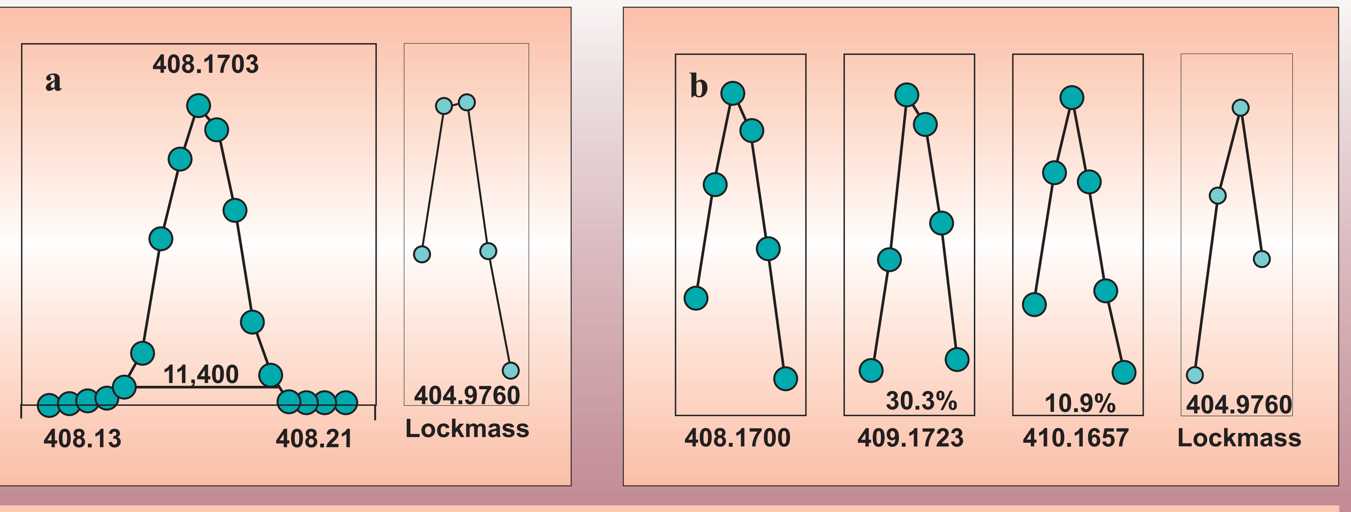


Figure 1. A full profile (a) and partial profiles (b).

3. Identification and Quantification of Aroclors

Aroclors are often identified from patterns of chromatographic peaks due to PCB isomers in an ECD chromatogram. When congener specific analyses are performed using mass spectrometric detection, Aroclors can be identified from the summed responses for each congener. Hence, chromatographic peak patterns and long analysis times should not be necessary to identify Aroclors.

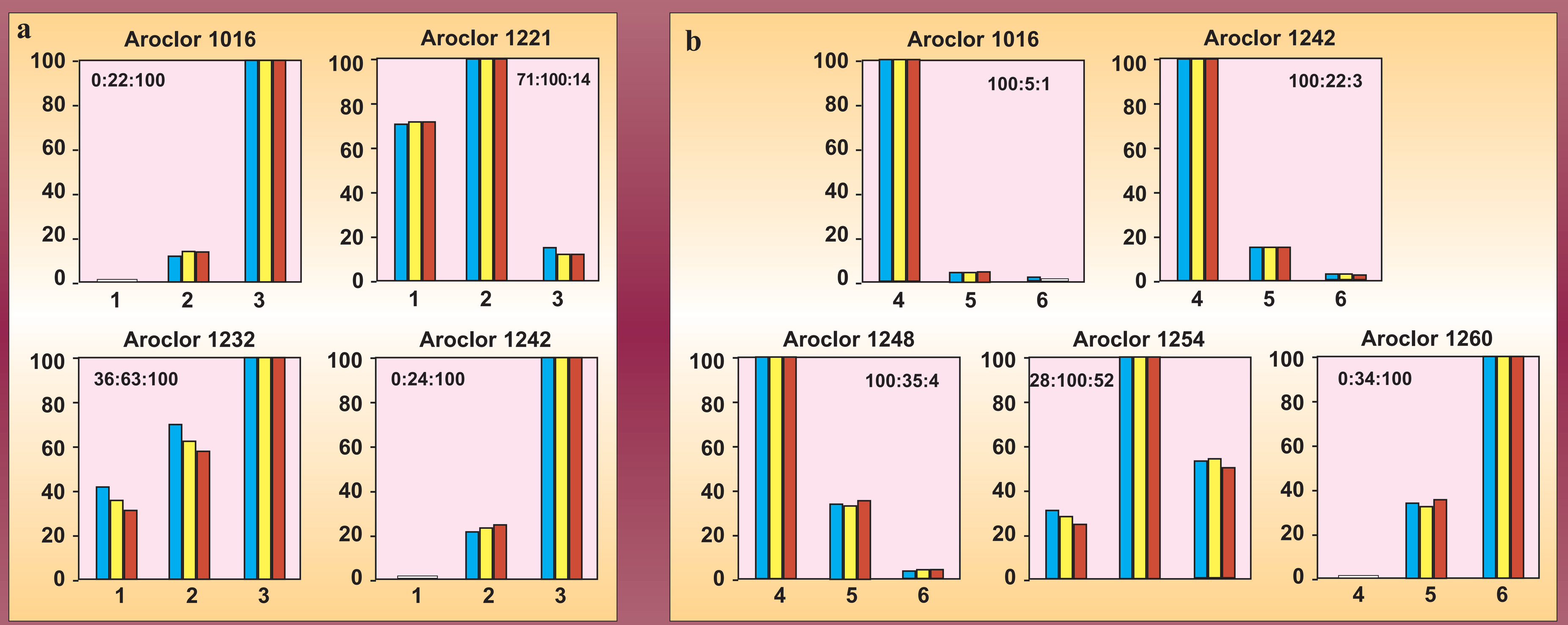
Two SIR descriptors were prepared to monitor 74% of the mass range for the profile of the most abundant molecular ion for three congeners: MonoCBs, DiCBs, and TriCBs, or TetraCBs, PentaCBs, and HexaCBs. A mass increment of 10 ppm between the m/z ratios was used with 15,000 resolution to ensure the partial profiles were well-centered in the observation windows, since a much wider mass range (70 Da) is needed to monitor three PCB congeners than for M, M+1 and M+2 profiles (7 Da, including the calibration ion). The congener distribution patterns in Figures 2a and 2b were observed when each Aroclor (10 ng in 1 µL of methylene chloride) was introduced by the probe, which was heated ballistically to 350°C. The standard deviations for triplicate determinations were less than the differences in the congener distributions between Aroclors. With probe introduction data acquired using both SIR descriptors, Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260 can be identified.

An analytical method can provide significantly different responses for different Aroclors. For accurate quantification, it can be necessary to use the correct Aroclor or mixture of Aroclors to prepare calibration standards. A commercial analytical lab determined that a sample extract contained 34% Aroclor 1254 and 66% Aroclor 1260 based on the peak areas of several PCB isomers in the ECD chromatogram. The PeCB:HxCB congener distribution observed with probe introduction was intermediate between Aroclors 1254 and 1260. Equation 1, a mass balance equation, was used to determine a relative response factor (1.07) between Aroclors 1254 and 1260 from a 50:50 mixture.

$$PeCB_{tot}/HxCB_{tot} = (PeCB_{54} + PeCB_{60})/(HxCB_{54} + HxCB_{60})$$
$$= (F_{Pe54}kf_{54} + F_{Pe60}(1-kf_{54}))/(F_{Hx54}kf_{54} + F_{hx60}(1-kf_{54})) \qquad \text{Equation 1}$$

Where: F_{Pe54} is the fraction of response due to PeCBs for Aroclor 1254; f_{54} is the fraction of Aroclor 1254 in the mixture; and k is the response due to PeCBs and HxCBs in Aroclor 1254 relative to Aroclor 1260.

Figure 2. Congener distributions for 7 Aroclors: (a) MonoCBs, DiCBs & TriCBs; (b) TetraCBs, PentaCBs & HexaCBs.



The factor k depends on the fraction of the total of congeners that are PeCBs or HxCBs and the instrumental response to those congeners for both Aroclors. With this factor, the same equation was then used to determine the fractions of the two Aroclors in 75:25 and 25:75 mixtures. The Aroclor 1254 fractions were in error by <2.5%. Similarly, the lab sample was estimated to contain 51% of Aroclor 1254 and 49% of Aroclor 1260.

A third SIR descriptor was used to quantify Aroclor 1254. Partial profiles were monitored for the most abundant molecular ion of the two most abundant congeners, PeCBs and HxCBs, and for a carbon labeled PeCB added as an internal standard. Triplicate data acquisitions were made for 1 µL of standard solutions containing 0.01 to 1000 ng of Aroclor 1254 and 1 ng of $^{13}C_{12}$-PeCB. Illustrated by Figure 3 is a useful calibration range of 5 orders of magnitude and linearity over 4 orders of magnitude. The lab estimated that the Aroclor mixture contained 2800 ppb of Aroclors; 1600 ppb was found by probe introduction. Because, the lab quantification method had a positive bias for Aroclor mixtures, the value from probe introduction was in reasonable agreement. Quantification against pure Aroclors and a 50:50 mixture yielded similar results (1600 - 2000 ppb), since the responses of the Aroclors were similar. A relative response factor near 1 might not be observed for other Aroclor mixtures.

Identification and quantification of Aroclors with probe introduction using MPPSIRD is feasible and provides several advantages over GC/HRMS analyses that require isomer separation:

1. ~10-fold faster analysis time
2. 5-fold better precision due to a data acquisition time of <1 min
3. a 5-10 times lower detection limit, since all isomers are monitored simultaneously
4. extreme simplicity
   a) no window defining mixtures are used to set start and end times for several SIR descriptors
   b) a single congener ratio and two exact masses replace retention time and ion ratio criteria for each isomer
   c) a single internal standard is used
   d) maintenance of good chromatographic conditions is not required

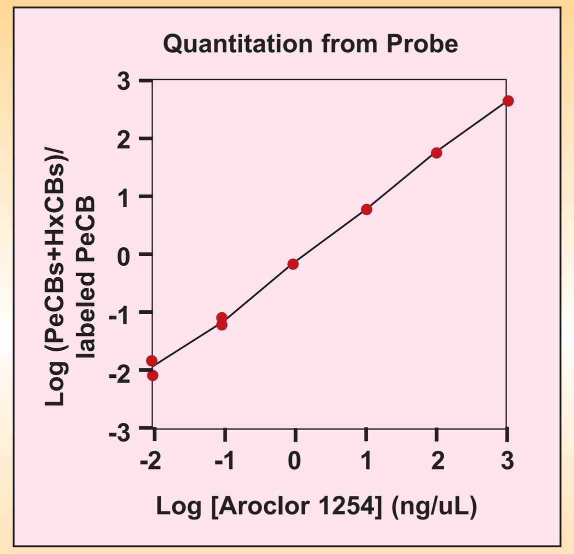
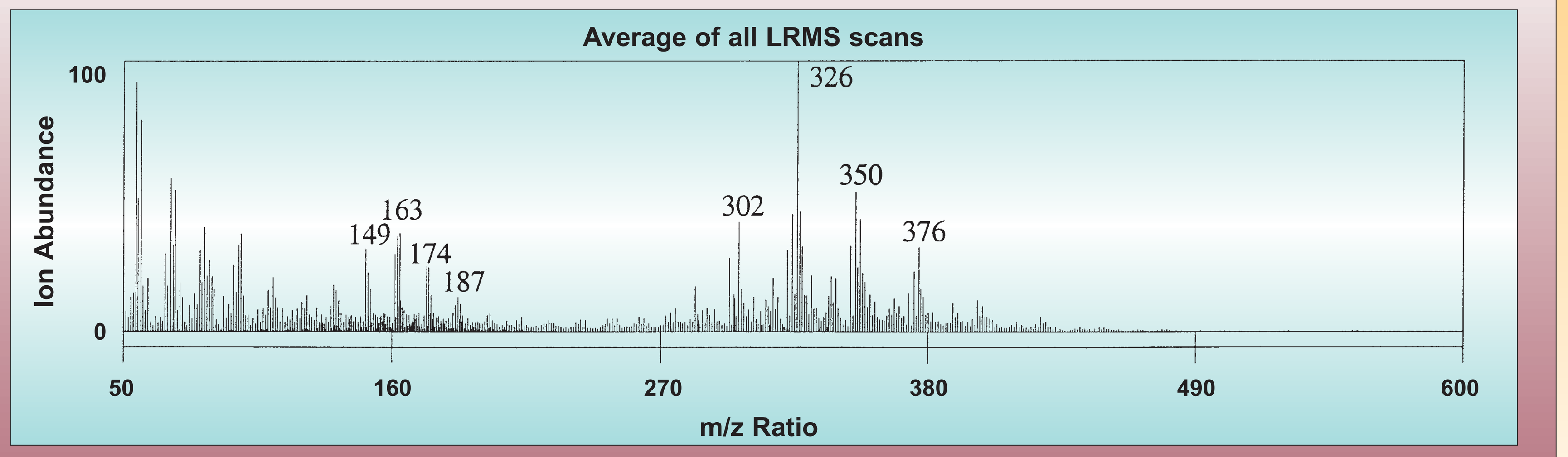


Figure 3. Log-Log plot of the signals corresponding to $\Sigma(PeCBs+HxCBs)/^{13}C_{12}$-PeCB.

Figure 4. Average low resolution mass spectrum as high molecular weight PAHs were volatilized from the probe.



4. Confirmation of High Molecular Weight PAHs

PAHs with masses up to 278 Da are analyzed by EPA method 8270 using GC/MS. Higher mass PAHs require long retention times and provide very broad peaks or do not elute as discrete chromatographic peaks from the GC column. Probe introduction permits screening for higher mass PAHs. Mass spectra for individual compounds are not observed, but an exact mass can be obtained for any ion observed in the composite mass spectrum. In Figure 4 is shown the average low resolution mass spectrum obtained as the PAHs in a 1 µL methylene chloride extract from a sample of a spent carbon electrode disposal site at an aluminum plant were volatilized from the probe.

The masses of the most abundant PAHs were greater than 278 Da and Method 8270 would underestimate the level of PAHs present. In Table 1 are listed the elemental compositions of 16 PAHs and the exact masses and mass errors determined for triplicate probe introductions. The last entry was not observed in any of the low resolution mass spectra; its probable existence was inferred from the PAH distribution. Thus, MPPSIRD provided greater sensitivity at 20,000 resolution, than the full scan mode at low resolution.

Other compositions containing O, N, P, or S atoms were possible based on these exact masses and error limits of ±2.5 ppm. Acquisition of M, M+1, and M+2 partial profiles did not provide data sufficient to exclude the other compositions, because other compounds (possibly PAHs having 2 more H atoms) produced ions that interfered with the M+2 profiles.

PAH	Exact Mass (Da)	Error (ppm)
$C_{24}H_{12}$	300.0944	+1.9
$C_{24}H_{14}$	302.1092	- 1.3
$C_{26}H_{14}$	326.1093	- 0.8
$C_{28}H_{14}$	350.1094	- 0.4
$C_{30}H_{14}$	374.1104	+ 2.2
$C_{30}H_{16}$	376.1254	+ 0.7
$C_{31}H_{18}$	390.1409	+ 0.1
$C_{32}H_{16}$	400.1258	+ 1.6
$C_{32}H_{18}$	402.1409	+ 0.1
$C_{34}H_{18}$	426.1409	+ 0.1
$C_{36}H_{18}$	450.1408	- 0.1
$C_{36}H_{20}$	452.1571	+ 1.5
$C_{38}H_{20}$	476.1562	- 0.6
$C_{40}H_{22}$	502.1727	+ 1.1
$C_{42}H_{22}$	526.1727	+ 1.1
$C_{44}H_{24}$	552.1878	+ 0.1

Table 1. PAHs, average exact masses, and mass errors.

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5. Determining Ionic Compositions for Components in a Complex Mixture

A methylene chloride extract of a black, viscous sample from a Superfund site was examined by GC/MS using MPPSIRD to determine elemental compositions for the molecular ion or other large mass ion for 47 components that provided chromatographic peaks. A three step process was used to determine compositions. A survey of profiles at each nominal mass was made across a 1600 ppm mass range using 3,000 resolution. Two or three points across each profile provided an estimate of the exact mass for the most abundant analyte ion observed in the low resolution mass spectrum. A better estimate of the exact mass was determined from the weighted average of several points near the apex of a full mass peak profile using data acquired at ~10,000 resolution across a mass range of 160 ppm. An example is shown in Figure 1a. Finally, at 20,000 resolution, M, M+1 and M+2 partial profiles like those in Figure 1b were plotted to provide the exact masses and relative abundances used to apply criteria. In Table 2 are listed several possible compositions and corresponding exact masses and relative abundance ranges that were calculated by a profile generation model[3] assuming the ion was composed of C, H, O, N, P, or S atoms. Each "X" indicates rejection of a composition based on the adjacent exact mass or relative abundance.

Table 2. Elemental compositions and quantities useful for distinguishing among them.

m/z 408.1700 ± 2.5 ppm — Up to: C34 H405 O25 N29 P13 S12 — Resolution: 20000

#	RDB	Composition	M	M+1	M+2	%M+1 Range	%M+2 Range
26	3.5	C17 H30 O8 N S	.1692	.1724	.1683 X	18.6 - 22.4 X	4.8 - 7.2 X
27	3.5	C17 H32 O6 N P2	.1705	.1738	.1762 X	17.3 - 21.8 X	0.0 - 2.0 X
28	8.5	C18 H26 O4 N5 S	.1706	.1734	.1689 X	20.0 - 25.1 X	4.8 - 6.7 X
29	2.5	C18 H34 O3 N S3	.1701	.1731	.1664	20.5 - 25.6 X	12.2 - 16.7 X
30	13.5	C20 H23 O N7 P	.1702	.1731	.1760 X	21.8 - 27.0 X	0.2 - 2.2 X
31	7.5	C20 H31 N3 P S2	.1697	.1727	.1663	22.2 - 27.5 X	8.4 - 11.2
32	8.0	C21 H29 O6 P	.1702	.1736	.1762 X	21.2 - 26.3 X	0.0 - 2.6 X
33	18.0	C24 H20 O N6	.1699	.1729	.1760 X	25.5 - 31.0	0.2 - 3.0 X
34	12.0	C24 H28 N2 S2	.1694	.1725	.1665	26.1 - 31.5	8.7 - 11.7
Experimental Values:			.1700	.1723	.1657	30.3	10.9

Probe introduction was used to search for 9 ions identified with GC introduction and to determine compositions of 4 additional ions. In Table 3 these ions and the number of criteria passed by the data obtained with both sample introduction techniques are listed. In general, interferences from other components in the extract reduced the number of useful criteria with probe introduction. Yet, unique compositions were determined for ions with masses less than 300 Da based on fewer than 5 criteria.

TIC Peak #	Nominal Mass	Composition	Criteria Met GC	Criteria Met Probe
9	141	$C_8H_{15}NO$	5	2
11	178	$C_{12}H_{18}O$	3	2
14	169	$C_{12}H_{11}N$	5	5
15	205	$C_{12}H_{15}NS$	5	4
16	192	$C_{12}H_{16}S$	5	2
27	246	$C_{14}H_{18}N_2S$	5	4
34	260	$C_{18}H_{16}N_2$	5	3
38	286	$C_{18}H_{26}ON_2$	5	3
44	326	$C_{18}H_{18}N_2S_2$	5	3[b]
	301	$C_{19}H_{13}N_2S$		3[a]
	365	$C_{21}H_{21}N_2S_2$		4[a]
	402	$C_{24}H_{22}N_2S_2$		4
	408	$C_{24}H_{28}N_2S_2$		5

[a] An absence of P atoms was assumed
[b] Insufficient to exclude all other compositions not containing P atoms

Table 3. Nominal masses, compositions and number of criteria passed with GC and probe introduction.

6. CONCLUSION

The high selectivity and sensitivity provided by MPPSIRD make rapid characterization from the probe feasible for both qualitative and quantitative applications. Although chromatographic separation is still necessary for some analytes in complex mixtures to determine the composition of the molecular ion with certainty, probe introduction with MPPSIRD is adequate to provide confirmation for the presence of target compounds without resort to more complex analyses.

[1]Grange, A.H.; Donnelly, J.R.; Brumley, W.C.; Billets, S.; Sovocool, G.W. Anal. Chem., 1994, 66, 4416-4421.
[2]Grange, A.H.; Donnelly, J.R.; Sovocool,G.W.; Brumley, W.C. Anal. Chem., 1996, 68, 553-560.
[3]Grange, A.H.; Brumley, W.C. Submitted to JASMS, 1996.

**A. Grange currently holds a National Research Council /NERL(CRD-LV) Senior Research Associateship.*

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